JC10 Rec'd PCT/PTO 12 DEC 2001

FORM PTO-1390 (REV. 9-2001) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: Mo-6837/LeA 33,565

U S APPLICATION NO (If known, see 37 CFR 1 5): To Be Assigned 10/018177

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/05036	02 June 2000 (2.06.00)	15 June 1999 (15.06.99)

TITLE OF INVENTION: POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES

APPLICANT(S) FOR DO/EO/US: ARNTZ, Hans-Detlef; BRECHT, Klaus; JOHN, Bernhard; SEIFERT, Peter and SCHNEIDER, Michael

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [X] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). .
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U S.C. 154(d)(4)
20. [X] Other items or information:

PTO Form 1449 w/references listed thereon

JC05 Rec'd PCT/PTO 12 DEC 2001

US APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To Be Assigned 10/018177	PCT/EP00/05036	Mo-6837/LeA 33,565

21. [X] The following fees are submitted:	CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x **$18.00**	$ 0.00	
Independent claims	1 - 3 =	0	x **$84.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$	

TOTAL OF ABOVE CALCULATIONS =	$ 890.00	
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +	$	
SUBTOTAL =	$ 890.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	$	
TOTAL NATIONAL FEE =	$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +	$ 40.00	
TOTAL FEES ENCLOSED =	$ 930.00	
Amount to be refunded:	$	
charged:	$	

a. [ ] A check in the amount of $ _____ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $ 930.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
Lyndanne M. Whalen
Bayer [illegible]
Patent [illegible]
100 Bayer Road
Pittsburgh, PA 15205-9741
USA

SIGNATURE

Lyndanne M. Whalen
NAME

29,457
REGISTRATION NUMBER

PATENT APPLICATION
Mo-6837
LeA 33,565

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF	)	
	)	PCT/EP00/05036
HANS-DETLEF ARNTZ ET AL	)	
	)	
SERIAL NUMBER: TO BE ASSIGNED	)	
	)	
FILED: HEREWITH	)	
	)	
TITLE: POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES	)	

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

Upon granting the enclosed application a Serial Number and filing date, please amend this application as follows:

"Express Mail" mailing label number ET700176545US
Date of Deposit December 12, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, ~~Washington, D.C. 20231~~ Arlington VA 22202

Donna J. Veatch
(Name of person mailing paper or fee)

(Signature of person mailing paper or fee)

IN THE TITLE:

At page 1, line 1, delete the title and substitute therefor - -POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES- -.

IN THE SPECIFICATION:

At page 1, line 3, please insert - - BACKGROUND OF THE INVENTION- -.

At page 2, above line 1, please insert - - SUMMARY OF THE INVENTION- -.

At page 2, lines 1-3, please amend the text to read as follows:

- -It has now been found that the addition of only 3 to 30 wt.%, based on total weight of polyether polyol component A1) and polyester polyol component A2), of specific polyesterpolyols to known polyetherpolyurethanes greatly improves their resistance to swelling in oil and petrol.- -

At page 2, line 4, please insert

- - BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph of the results of the sterile hydrolysis test conducted on specimens aged at 70°C and 95% relative humidity for a period of 7-14 days.

DETAILED DESCRIPTION OF THE INVENTION- - .

At page 2, lines 27-29, please amend the text to read as follows:

- -Polyetherpolyol component A1) has a number average molecular weight of 1000 to 8000 g/mol and has a hydroxyl functionality of 2.0 or is substantially a mixture with an average hydroxyl functionality of 2.02 to 2.95 composed of- -

At page 7, lines 15-17, please amend the text to read as follows:

- -The grades of PUR obtained are suitable in particular for preparing soles of shoes which comply with safety shoe standard EN 344, but may also be used for wheels, rollers, flexible tubing and tires due to their ability to withstand a high degree of stress.- -

IN THE CLAIMS:

Please cancel Claims 1-10 and add the following new Claims 11- 22:

- -11. A process for the production of oil and petroleum-resistant (polyurea)polyurethanes comprising reacting a mixture comprising

A1) a polyether polyol component having a number average molecular weight of from 1000 to 8000 g/mol,

A2) from 3 to 30 wt.%, based on total weight of components A1) and A2), of a polyester polyol component having a number average molecular weight of from 1000 to 6000 g/mol,

B) a polyisocyanate component,

C) a chain extending agent,

and optionally,

D) a blowing agent and/or

E) an activator, auxiliary substance or additive

at an isocyanate index of from 70 to 130.

12. The process of Claim 11 in which the polyester polyol component comprises

(1) from 20 to 47.3 mol% of units derived from adipic acid,

(2) from 0-20 mol% of units derived from glutaric acid,

(3) from 0 to 10 mol% of units derived from succinic acid,

(4) from 10 to 30 mol% of units derived neopentyl glycol,

(5) from 10-30 mol% of units derived from hexanediol,

(6) from 0-15 mol% of units derived from ethanediol,

and (7) from 10-20 mol% of units derived from butanediol.

13. The process of Claim 12 in which the polyester polyol component is included in the polyisocyanate component.

14. The process of Claim 11 in which the polyester polyol component is included in the polyisocyanate component.

15. The process of Claim 11 in which the polyether polyol component, polyester polyol component, chain extending agent, any blowing agent and any activator, auxiliary substance or additive are combined before being reacted with the polyisocyanate component.

16. The oil and petroleum-resistant (polyurea)polyurethane of Claim 12.

17. The oil and petroleum-resistant (polyurea)polyurethane of Claim 11.

18. The (polyurea)polyurethane of Claim 17 which is transparent.

19. The (polyurea)polyurethane of Claim 17 which is resistant hydrolysis and microbial action.

20. A shoe sole composed of the (polyurea)polyurethane of Claim 17.

21. Safety clothing produced from the (polyurea)polyurethane of Claim 17.

22. Flexible tubing produced from the (polyurea)polyurethane of Claim 17.- -

IN THE ABSTRACT:

Please delete the existing Abstract Page and add the following new Abstract page.

--POLYUREA POLYURETHANES HAVING
IMPROVED PHYSICAL PROPERTIES

ABSTRACT OF THE DISCLOSURE

A process for preparing oil and petroleum-resistant cellular to solid (polyurea)polyurethanes (PURS) with improved physical properties in which a polyether polyol component having a number average molecular weight of from 1000 to 8000 and a polyester polyol component having a number average molecular weight of from 1000 to 6000 are reacted with a polyisocyanate and the (polyurea) polyurethanes produced by that process. The (polyurea)polyurethanes are particularly useful for personal safety equipment and in the construction of automobiles.- -

REMARKS

The title has been changed at page 1 and on the Abstract page to make it correspond to the title given on the Declaration and Assignment signed by the inventors. A new Abstract page is included herewith.

The specification has been amended at pages 1 and 2 to insert the headings "BACKGROUND OF THE INVENTION", "SUMMARY OF THE INVENTION", "BRIEF DESCRIPTION OF THE DRAWING" AND "DETAILED DESCRIPTION OF THE INVENTION".

The specification has been amended at page 2, lines 1-3 to recite the basis for the 3-30 wt% recited.

The specification has also been amended at page 2 to insert a description of Figure 1. Support for this description is found at page 11, lines 1-2 of the specification.

The specification has further been amended at page 2 to change "consisting of" to "composed of" to make this section of specification consistent with the remainder of the specification and the claims.

Claims 1-10 have been cancelled.

New Claim 11 corresponds substantially to original Claim 1.

New Claim 12 corresponds substantially to original Claim 2.

New Claims 13 and 14 are directed to the subject matter of original Claim 3.

New Claim 15 corresponds substantially to original Claim 4.

New Claims 16 and 17 are directed to the subject matter of original Claim 5.

New Claim 18 corresponds substantially to original Claim 6.

New Claim 19 corresponds substantially to original Claim 7.

New Claim 20 corresponds substantially to original Claim 8.

New Claim 21 corresponds substantially to original Claim 9.

New Claim 22 is directed to flexible tubing, one of the embodiments of the invention as claimed in original Claim 10.

The Abstract has been revised to place it in better form.

Entry of this Amendment and an action on the merits of this case are respectfully requested.

Respectfully submitted,

By _____
Lyndanne M. Whalen
Attorney for Applicants
Reg. No. 29,457

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s:/sr/lmw0227

VERSION WITH MARKINGS TO SHOW CHANGES MADE:

IN THE TITLE:

At page 1, line 1, the title has been deleted and the following new title inserted therefor: - -POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES- -.

IN THE SPECIFICATION:

At page 1, line 3, - - BACKGROUND OF THE INVENTION- - has been inserted.

At page 2, above line 1, - - SUMMARY OF THE INVENTION- - has been inserted.

At page 2, lines 1-3, the text has been amended as follows:

It has now been found that the addition of only 3 to 30 wt.%, based on total weight of polyether polyol component A1) and polyester polyol component A2), of specific polyesterpolyols to known polyetherpolyurethanes greatly improves their resistance to swelling in oil and petrol.- -

At page 2, line 4, the following has been inserted:

- - BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph of the results of the sterile hydrolysis test conducted on specimens aged at 70°C and 95% relative humidity for a period of 7-14 days.

DETAILED DESCRIPTION OF THE INVENTION- - .

At page 2, lines 27-29, the text has been amended as follows:

- -Polyetherpolyol component A1) has a number average molecular weight of 1000 to 8000 g/mol and has a hydroxyl functionality of 2.0 or is substantially a mixture with an average hydroxyl functionality of 2.02 to 2.95[, consisting of] composed of- -

At page 7, lines 15-17, the text has been amended as follows:

- -The grades of PUR obtained are suitable in particular for preparing soles of shoes which comply with safety shoe standard EN 344, but may also be used for wheels, rollers, flexible tubing and [tyres]tires due to their ability to withstand a high degree of stress.- -

IN THE CLAIMS:

Claims 1-10 have been cancelled and the following new Claims 11- 22 have been added:

- -11. A process for the production of oil and petroleum-resistant (polyurea)polyurethanes comprising reacting a mixture comprising

A1) a polyether polyol component having a number average molecular weight of from 1000 to 8000 g/mol,

A2) from 3 to 30 wt.%, based on total weight of components A1) and A2), of a polyester polyol component having a number average molecular weight of from 1000 to 6000 g/mol,

B) a polyisocyanate component,

C) a chain extending agent,

and optionally,

D) a blowing agent and/or

E) an activator, auxiliary substance or additive

at an isocyanate index of from 70 to 130.

12. The process of Claim 11 in which the polyester polyol component comprises

(1) from 20 to 47.3 mol% of units derived from adipic acid,

(2) from 0-20 mol% of units derived from glutaric acid,

(3) from 0 to 10 mol% of units derived from succinic acid,

(4) from 10 to 30 mol% of units derived neopentyl glycol,

(5) from 10-30 mol% of units derived from hexanediol,

(6) from 0-15 mol% of units derived from ethanediol,

and (7) from 10-20 mol% of units derived from butanediol.

13. The process of Claim 12 in which the polyester polyol component is included in the polyisocyanate component.

14. The process of Claim 11 in which the polyester polyol component is included in the polyisocyanate component.

15. The process of Claim 11 in which the polyether polyol component, polyester polyol component, chain extending agent, any blowing agent and any activator, auxiliary substance or additive are combined before being reacted with the polyisocyanate component.

16. The oil and petroleum-resistant (polyurea)polyurethane of Claim 12.

17. The oil and petroleum-resistant (polyurea)polyurethane of Claim 11.

18. The (polyurea)polyurethane of Claim 17 which is transparent.

19. The (polyurea)polyurethane of Claim 17 which is resistant hydrolysis and microbial action.

20. A shoe sole composed of the (polyurea)polyurethane of Claim 17.

21. Safety clothing produced from the (polyurea)polyurethane of Claim 17.

22. Flexible tubing produced from the (polyurea)polyurethane of Claim 17.- -

IN THE ABSTRACT:

The Abstract page has been amended as follows:

-- POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES[Polyurethanes with improved physical properties].

[The invention provides a] A process for preparing oil and petroleum-resistant cellular to solid (polyurea)polyurethanes (PURS) with improved physical properties[,] in which a polyether polyol component having a number average molecular weight of from 1000 to 8000 and a polyester polyol component having a number average molecular weight of from 1000 to 6000 are reacted with a polyisocyanate and the (polyurea)polyurethanes produced by that process. [such as are required, for example,] The (polyurea)polyurethanes are particularly useful for personal safety equipment and in the construction of automobiles.

Polyureapolyurethanes with improved physical properties

Abstract

The invention provides a process for preparing oil and petrol-resistant cellular to solid (polyurea)polyurethanes (PURs) with improved physical properties, such as are required, for example, for personal safety equipment and in the construction of automobiles.

Polyureapolyurethanes with improved physical properties

The invention provides a process for preparing oil and petrol-resistant cellular to solid (polyurea)polyurethanes (PURs) with improved physical properties, such as are required for personal safety equipment and for the construction of automobiles.

The wide variety of polyurethane plastics, their structure and methods of preparation has represented the prior art for many years. WO 98/23659 describes polyetherpolyurethanes which are relatively petrol-resistant. However, these swell in an obvious manner on contact with hydrocarbons and thus their mechanical and physical properties become modified. In addition, when processing polyetherpolyurethanes to produce moulded articles, the moulds become heavily soiled.

The polyester-PURs generally used hitherto in such applications have the following disadvantages:

- the high viscosity of the components when ready for processing leads to problems with the accurate reproducibility of moulded articles;
- the temperatures of 40-60°C required for processing reduces the useful lifetime of the system components;
- inadequate resistance to hydrolysis and microbes leads to a limited operational lifetime for the products;
- the ability to control the polyaddition reaction by catalysts is restricted since these often promote glycolysis of the ester.

It has now been found that the addition of only 3 to 30 wt.% of specific polyesterpolyols to known polyetherpolyurethanes greatly improves their resistance to swelling in oil and petrol.

The invention provides oil and petrol-resistant cellular to solid (polyurea)polyurethanes, obtainable by reacting a reaction mixture comprising

A1) a polyetherpolyol component with a number average molecular weight of 1000 to 8000 g/mol, preferably 2000 to 6000 g/mol,

A2) a polyesterpolyol component with a number average molecular weight of 1000 to 6000 g/mol, preferably 1000 to 4000 g/mol,

B) a polyisocyanate component,

C) chain-extending agents,

optionally

D) blowing agents and

E) activators and other auxiliary substances and additives,

wherein the starting materials are reacted while maintaining the isocyanate index at a value of 70 to 130.

Polyetherpolyol component A1) has a number average molecular weight of 1000 to 8000 g/mol and has a hydroxyl functionality of 2.0 or is substantially a mixture with an average hydroxyl functionality of 2.02 to 2.95, consisting of

a) at least one polyetherdiol with a hydroxyl value in the range 10 to 115, which has been prepared by propoxylation of a difunctional starter and subsequent ethoxylation of the propoxylation product while maintaining a ratio by weight of propylene oxide to ethylene oxide of 60:40 to 85:15 and

b) at least one polyethertriol with a hydroxyl value in the range 12 to 56, which has been prepared by propoxylation of a trifunctional starter and subsequent ethoxylation of the propoxylation product while maintaining a ratio by weight of propylene oxide to ethylene oxide of 60:40 to 85:15 and which optionally contains fillers based on styrene/acrylonitrile copolymers, polyureas or polyhydrazocarbonamides in an amount of up to 20 wt.%, with respect to the total weight of component b).

Suitable compounds for use as component A2) are polyesterpolyols with a number average molecular weight of 1000 to 6000 g/mol, which have been prepared, for example, from organic dicarboxylic acids with 2 to 12 carbon atoms, preferably aliphatic dicarboxylic acids with 4 to 6 carbon atoms and polyhydric alcohols, preferably diols, with 2 to 12 carbon atoms, preferably 2 carbon atoms. Suitable dicarboxylic acids are, for example: succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids may be used individually or in a mixture with each other. Instead of the free dicarboxylic acids, the corresponding dicarboxylic acid derivatives, such as e.g. the monoesters and/or diesters of dicarboxylic acids with alcohols with 1 to 4 carbon atoms or dicarboxylic acid anhydrides, may be used. Dicarboxylic acid mixtures of succinic, glutaric and adipic acids in the ratio of, for example, 20 to 35 parts by wt. of succinic acid to 35 to 50 parts by wt. of glutaric acid to 20 to 32 parts by wt. of adipic acid are preferably used. The use of adipic acid is particularly preferred. Examples of dihydric and polyhydric alcohols, in particular diols and alkylene glycols, are: ethanediol, diethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, methylpropane-1,3-diol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl

glycol, 1,10-decanediol, glycerol, trimethylolpropane and pentaerythritol. 1,2-ethanediol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane or mixtures of at least two of the diols mentioned are preferred, in particular mixtures of ethanediol, diethylene glycol, 1,4-butanediol, isobutyl glycol, 1,3-propanediol, 1,2-propanediol, neopentyl glycol, 1,6-hexanediol, glycerol and/or trimethylolpropane. Furthermore, polyesterpolyols formed from lactones, e.g. ε-caprolactone, or hydroxycarboxylic acids, e.g. o-hydroxycaproic acid and hydroxyacetic acid, may also be used.

To prepare the polyesterpolyols, the organic, e.g. aromatic and preferably aliphatic polycarboxylic acids and/or derivatives of these and polyhydric alcohols are polycondensed without the use of a catalyst or in the presence of esterification catalysts, expediently in an atmosphere of inert gases, such as e.g. nitrogen, carbon monoxide, helium, argon, or also in the molten state at temperatures of 150 to 300°C, preferably 180 to 230°C, optionally under reduced pressure, until the acid value required is reached, this being advantageously less than 10 and preferably less than 1.

According to a preferred embodiment, the esterification mixture is polycondensed at the temperatures mentioned above until reaching an acid value of 80 to 30, preferably 40 to 30, under atmospheric pressure and then under a pressure of less than 500 mbar, preferably 10 to 150 mbar. Suitable esterification catalysts are, for example, iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metal, metal oxides or metal salts. Polycondensation may also be performed in the liquid phase, however, in the presence of diluents and/or entraining agents such as e.g. benzene, toluene, xylene or chlorobenzene, for azeotropic distillation of the condensation water.

To prepare the polyesterpolyols, the organic polycarboxylic acids and/or derivatives are advantageously polycondensed with polyhydric alcohols in the ratio by moles of 1 : 1 to 1.8, preferably 1 : 1.05 to 1.2. The polyesterpolyols obtained preferably have

a functionality of 2 to 3, in particular 2 to 2.6 and a number average molecular weight of 400 to 6000, preferably 800 to 3500.

Suitable polyesterpolyols are also polycarbonates which contain hydroxyl groups. Suitable polycarbonates which contain hydroxyl groups are those of a type known per se which can be prepared, for example, by reacting diols such as 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, trioxyethylene glycol and/or tetraoxyethylene glycol with diaryl carbonates, e.g. diphenyl carbonate or phosgene.

Polyesterpolyols with the following composition (compounds from which the building blocks of repeating units in the polyol are derived are cited) are particularly suitable for preparing (polyurea)polyurethanes according to the invention:

adipic acid	20-50 mol.%, preferably 40-48 mol.%
glutaric acid	0-20 mol.%, preferably 0 mol.%
succinic acid	0-10 mol.%, preferably 0 mol.%
neopentyl glycol	10-30 mol.%, preferably 19-23 mol.%
hexanediol	10-40 mol.%, preferably 30-35 mol.%
ethanediol	0-15 mol.%, preferably 0-5 mol.%
butanediol	10-20 mol.%, preferably 0-5 mol.%

Polyesterpolyols with the following compositions are preferably used:

1. 47.1 mol.% adipic acid, 19.4 mol.% neopentyl glycol, 30.6 mol.% hexanediol, 2.9 mol.% butanediol;

2. 47.1 mol.% adipic acid, 19.4 mol.% neopentyl glycol, 30.6 mol.% hexanediol, 2.9 mol.% ethanediol;

3. 47.1 mol.% adipic acid, 19.4 mol.% neopentyl glycol, 30.1 mol.% hexanediol, 1.7 mol.% butanediol, 1.7 mol.% ethanediol.

Polyesterpolyols with this composition are miscible with the polyetherpolyols described under A1) over wide limits and exhibit no tendency to separate. In contrast to this, commercially available ethanediol/butane-1,4-diol/polyadipates (e.g. Bayflex® 2002H, Bayer AG) begin to separate out above a concentration of 5 wt.% in the polyetherpolyols mentioned.

As a result of adding these polyesterpolyols, the physical and mechanical properties of the PURs are affected positively without the negative properties of polyesterpolyols being detectable. The use of these esters which are compatible with polyetherpolyols enables targeted optimisation of the properties of (polyurea)polyurethanes according to the invention since polyol mixtures can be used which contain between 0 and 100% of ethers and correspondingly between 100 and 0% of esters, preferably 70 to 95 wt.% of ethers and 5 to 30 wt.% of esters. Another advantage is that transparent materials can be prepared with these types of polyol mixtures in any of these compositions.

Compounds for use as component B) are industrially readily accessible polyisocyanates such as diisocyanatodiphenylmethane, toluene diisocyanate and mixtures of these with partially carbodiimidised isocyanates in pre-extended form with an NCO content of 5 to 30 wt.%. Polyethers or polyesters or mixtures with the structure described under components A1) and A2) which have a hydroxyl functionality of 2 to 2.5 are used for pre-extension purposes.

Compounds for use as component C) are ethanediol, diethylene glycol, butanediol, methylpropanediol, propylene glycol, triethanolamine, glycerol, diaminoethyltoluylene or mixtures of these compounds. Compounds for use as component D) are optionally water and/or a physical blowing agent, e.g. R 134a (a mixture of hydrofluoroalkanes).

Catalysts and optionally incorporated auxiliary substances and additives E) which may be used are activators such as e.g. tertiary amines, tin or titanium compounds and, depending on the requirements, surface active substances, foam stabilisers, cell regulators, internal mould release agents, colorants, pigments, anti-hydrolysis agents, substances which prevent the growth of fungi and bacteria, oxidising agents, light protection agents and antistatic agents, which are disclosed in the literature.

(Polyurea)polyurethanes according to the invention are prepared by methods known in principle by a person skilled in the art. In general, components A) and C) to E) are combined with a polyol component and reacted in a one-stage reaction with isocyanate component B), wherein conventional two-component mixing units may be used. Component A2) may be a constituent of both the polyol component and the isocyanate component.

The grades of PUR obtained are suitable in particular for preparing soles of shoes which comply with safety shoe standard EN 344, but may also be used for wheels, rollers and tyres due to their ability to withstand a high degree of stress.

Examples 1 - 6

Starting materials

Polyhydroxyl compounds A

A1: Propylene oxide/ethylene oxide random block polyether started with trimethylolpropane and propylene glycol; OH value 28; functionality 2.1;

A2a: Ethanediol/butane-1,4-diol/polyadipate; OH value 56; functionality 2;

A2b: Polyersterpolyol containing 47.1 mol.% of units derived from adipic acid, 19.4 mol.% of units derived from neopentyl glycol, 30.6 mol.% of units derived from hexanediol and 2.9 mol.% of units derived from butanediol;

Polyisocyanate B

B: Soft segment pre-polymer with a number average molecular weight of 4000, the reaction product of MDI with TPG and a PO/EO random block polyetherdiol, NCO value: 17 wt.%;

Chain-extending agent C

Butanediol;

Catalyst E

Mixture of diazabicyclooctane (DABCO) and dibutyltin dilaurate (DBTDL) in a ratio of about 96:4.

Method used

Components A1, A2 and C were mixed in accordance with the data in table 1 and reacted with isocyanates B1 or B2 in a conventional two-component mixing and metering unit by the low pressure method and introduced into an aluminium mould, the surface of which had not been treated in any way nor provided with external mould release agents. After a reaction time of 2.5 to 4 minutes, the moulded item was removed. The mechanical properties were determined 48 hours after producing test plates (200 x 200 x 10 mm^3), from which conventional test specimens were prepared and measured as described in the standards (DIN 53504 S1 rod, DIN 53507 tear propagation resistance, abrasion DIN 53516; oil and petrol resistance DIN EN 344). The results are summarised in table 1.

Table 1

Example	1*	2	3	4	5	6
A1 [wt.%]	91.3	81.27	81.27	71.27	61.27	47.18
A2a [wt.%]	-	10.0	-	-	-	-
A2b [wt.%]	-	-	10.0	20.0	30.0	40.0
C [wt.%]	8.0	8.0	8.0	8.0	8.0	12.0
E [wt.%]	0.73	0.73	0.73	0.73	0.73	0.52
D: water [wt.%]	-	-	-	-	-	0.3
Phase-stable	yes	no	yes	yes	yes	yes
B [wt.%]	55	55	55	54	53	89
Bulk density [kg/m^3]	950	950	950	950	950	600
Hardness [Shore A]	60	60	60	60	60	55
Tensile strength [MPas]	9.5	10.0	9.9	11.5	9.1	5.4
Elongation at break [%]	660	630	640	610	550	520
Tear propagation resist. [kN/m]	13.5	12.0	13.2	12.9	12.2	6.5
Abrasion [mg]	150	140	130	120	105	180
Volume change in isooctane [%]	11	10	9	6	3.5	11

* Comparison example, not in accordance with the invention

Whereas with conventional ester formulations, the moulds have to be cleansed weekly, when processing polyether formulations it is conventional to cleanse the moulds daily. With the new hybrid formulations, about 800 mould release operations can be performed without any detectable build-up in the moulds, which corresponds approximately to a cleansing cycle of 4 days.

In a test where articles were buried in soil under defined conditions (30°C, 95% rel. humidity, in humus soil enriched with moulds, for 8 weeks), it can be shown that addition of the ester does not impair the long-term resistance to microbial degradation. Pure esterpolyurethanes have obvious cracks in the surface of the material after four weeks under these conditions. Similar positive results were

obtained in a sterile hydrolysis test in which the specimens were aged at 70°C, 95% rel. humidity for a period of 7 to 14 days (fig. 1).

In trials with various shapes of moulds for soles, a decrease in the frequency of bubbles in the frame region of the sole was observed when pure polyether formulations were replaced by higher viscosity ether/ester formulations.

Claims

1. A process for preparing oil and petrol-resistant cellular to solid (polyurea)polyurethanes by reacting a reaction mixture comprising

A1) a polyetherpolyol component with a number average molecular weight of 1000 to 8000 g/mol,

A2) 3-30% of a polyesterpolyol component with a number average molecular weight of 1000 to 6000 g/mol,

B) a polyisocyanate component,

C) chain-extending agents,

optionally

D) blowing agents and

E) activators and other auxiliary substances and additives,

wherein the starting materials are reacted while maintaining the isocyanate index at a value of 70 to 130.

2. A process according to Claim 1, in which component A2) contains a polyesterpolyol which contains 20-47.3 mol.% of units derived from adipic acid, 0-20 mol.% of units derived from glutaric acid, 0-10 mol.% of units derived from succinic acid, 10-30 mol.% of units derived from neopentyl glycol, 10-30 mol.% of units derived from hexanediol, 0-15 mol.% of units derived from ethanediol and 10-20 mol.% of units derived from butanediol.

3. A process according to Claim 1 or 2, in which component A2) is used as a constituent of polyisocyanate component B).

4. A process according to Claim 1 or 2, in which components A1), A2), C) and optionally D) and E) are combined to give a polyol component which is reacted with polyisocyanate component B).

5. Oil and petrol-resistant cellular to solid (polyurea)polyurethanes obtainable according to any one of Claims 1 to 4.

6. Transparent (polyurea)polyurethanes according to Claim 5.

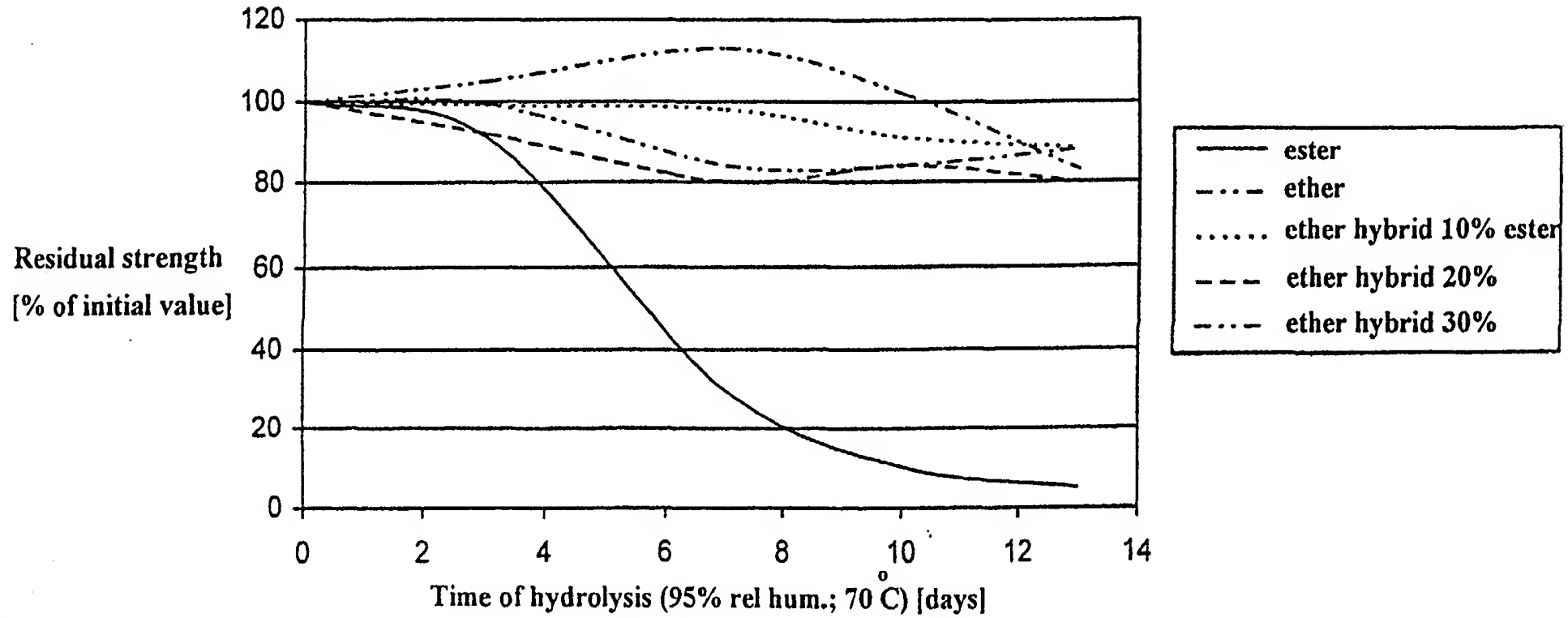
7. Materials containing (polyurea)polyurethanes according to Claim 5 or 6 which are resistant to hydrolysis and the action of microbes.

8. Shoe soles containing (polyurea)polyurethanes according to Claim 5 or 6.

9. Use of (polyurea)polyurethanes according to with Claim 5 or 6 for the production of safety clothing.

10. Use of (polyurea)polyurethanes according to Claim 5 or 6 in the construction of cars.

Figure 1



COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

POLYUREA POLYURETHANES HAVING IMPROVED PHYSICAL PROPERTIES

the specification of which is attached hereto,

or was filed on **June 2, 2000**

as a PCT Application Serial No. **PCT/EP00/05036**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 27 188.7	**Germany**	**June 15, 1999**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occured between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

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